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TI - Amorphous copper silicates, their manufacture, and their uses in antibacterial agents and antifouling coatings

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SO - Jpn. Kokai Tokkyo Koho, 8 pp.

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PATENT NO. KIND DATE APPLICATION NO. DATE

PN - JP8283013 A 19961029 JP 1995-111088 19950413 <--

PR - JP 1995-111088 19950413

AB - The silicates satisfy CuO/SiO₂ mol. compn. 0.5-2, BET sp. surface area 100-300 m²/g, oil absorption 50-130 mL/100 g, and Cu ion elution to 1 N NH₄OH per total Cu .ltoreq. 1.5% and are manufd. by stirring aq. alkali silicate solns. having SiO₂ solid concn. 0.1-6% with aq. Cu salt solns. to satisfy the above CuO/SiO₂ mol compn. at 20-60.degree. and reaction finish pH 6.8-7.5, and washing the products at pH 6.5-8.5. Cu ion is slowly discharged from the silicates to aq. media and the silicates are utilized for the low-cost antibacterial agents and coatings.

ST - amorphous copper silicate manuf antibacterial; bactericide amorphous copper silicate manuf; antifouling coating amorphous copper silicate manuf

IT - Antibacterial agents
(amorphous copper silicates and their manuf. for antibacterial agents and antifouling coatings)

IT - Coating materials
(antifouling; amorphous copper silicates and their manuf. for antibacterial agents and antifouling coatings)

IT - 1344-72-5P, Copper silicate
RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(amorphous copper silicates and their manuf. for antibacterial agents and antifouling coatings)

IT - 1312-76-1, Potassium silicate 1344-09-8, Sodium silicate 1344-67-8, Copper chloride 4180-12-5, Copper acetate 10124-44-4, Sulfuric acid copper salt 10402-29-6, Copper nitrate

RL: RCT (Reactant); RACT (Reactant or reagent)
(amorphous copper silicates and their manuf. for antibacterial agents and antifouling coatings)

+ Category
Tokyo IP firm -
→ FP27328
FP2834-

Fe silicate, purifying performance for all of HC, CO and NOX is improved. Ion exchange method, impregnation method or the like is elected as a method for carrying Cu.

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CLAIMS

[Claim(s)]

[Claim 1] CuO/SiO₂ of oxide criteria Amorphous silicic-acid copper whose oil absorption the range of 0.5 thru/or 2 has the mol presentation to express, and a BET specific surface area is 50 thru/or 130ml / 100g in 100 thru/or 300m² / g and whose elution volume of the copper ion by the aqueous ammonia of 1 convention is 1.5% or less per all Cu(s).

[Claim 2] Amorphous silicic-acid copper according to claim 1 whose pH of 25-degree C 5% aqueous suspension the bulk density of the above-mentioned silicic-acid copper is 6 thru/or 8.5 in ml in 0.5 thru/or 0.8g /.

[Claim 3] Amorphous silicic-acid copper according to claim 1 whose solubility in the aqueous medium of pH6 thru/or 8.5 range the above-mentioned silicic-acid copper is 1 ppm or less as Cu ion.

[Claim 4] SiO₂ the alkali silicic acid water solution whose solid content concentration be 0.1 thru/or 6 % of the weight -- the water solution of copper salt -- CuO/SiO₂ the quantitative ratio from which a mol presentation serve as the range of 0.5 thru/or 2 -- the bottom of temperature 20 thru/or a 60 - degree C condition -- and the manufacture approach of the amorphous silicic acid copper characterize by pour into the bottom of churning and rinse the product obtain on condition that pH6.5 thru/or 8.5 so that the reaction termination pH may turn to 6.8 thru/or 7.5.

[Claim 5] The manufacture approach of silicic-acid copper according to claim 4 of a copper nitrate, a copper sulfate, a copper chloride, and copper acetate that the above-mentioned copper salt is any one or more sorts of water solutions at least.

[Claim 6] The antimicrobial agent which contains amorphous silicic-acid copper given

in any [claim 1 thru/or] of 3 they are, and changes.

[Claim 7] The antifouling paint which contains amorphous silicic-acid copper given in any [claim 1 thru/or] of 3 they are, and changes.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the amorphous silicic-acid copper which was excellent in sustained-release [of a copper ion] at the detail, and its process more about amorphous silicic-acid copper, its process, and its application. This invention relates to amorphous silicic-acid copper useful especially as an antimicrobial agent and an antifouling paint, and its process.

[0002]

[Description of the Prior Art] Although several sorts of things (Shattuckite, Plancheite, Dioptase, Chrysocolla) produced naturally are known as a copper silicate mineral In reports (403-414 pages of the 6 volume [of a mineralogy magazine / 12th] No., May, 1976), such as Kawamura A copper sulfate, silica gel, and copper carbonate are used as a raw material, and it is 2000kg/cm² at 350 degrees C. Having compounded plan HEAITO (Cu₇ Si₈O₂₂(OH)₂ · 3H₂O) by hydrothermal synthesis is reported.

[0003] Since a copper ion has antibacterial, the antibacterial silicate which comes to permute some metals [at least] which there are many proposals also about using the silicate containing copper for an antimicrobial agent or an antifouling paint, for example, are contained in a stratified silicate at JP,3-193707,A, and in which the ion exchange is possible with the coordination compound of a copper ion and an organic ligand is indicated.

[0004] Moreover, the antibacterial constituent which prepared the coat of the aluminosilicate containing antibacterial metal ions, such as copper, in JP,3-252308,A on the surface of silica gel is indicated.

[0005] Furthermore, the crystalline copper silicate which has ZSM-5 similar structure and the copper and alkaline earth metal of the amount of requests distributed to altitude in the crystal is indicated by JP,4-182312,A.

[0006]

[Problem(s) to be Solved by the Invention] However, by composition of conventional silicic-acid copper, it is 1000kg/cm². Since several days are needed for composition

while needing the above high pressure, there is still a difficulty in industrial manufacture. Moreover, the concentration of the copper component which can be introduced by the approach of introducing a copper ion into a stratified silicate mineral by the ion exchange and the approach of covering a copper content compound on the front face of support is low, and dissatisfied too in respect of effectiveness, such as antibacterial.

[0007] When this invention persons hydrolyzed water-soluble copper salt and silicic-acid alkali under specific conditions, it found out the amorphous silicic-acid copper which contains a copper component by high concentration being obtained, and this amorphous silicic-acid copper being excellent in sustained-release [of a copper ion], and excelling also in durability, such as antibacterial.

[0008] That is, the purpose of this invention is to offer amorphous silicic-acid copper with the large content of a copper component especially amorphous silicic-acid copper excellent in sustained-release [of a copper ion], and its process. Moreover, other purposes of this invention are comparatively on mild conditions to offer the approach that amorphous silicic-acid copper can be manufactured to the inside of a short time, without needing the hydrothermal processing in high pressure. The purpose of further others of this invention is to offer an antimicrobial agent and an antifouling paint excellent in the durability of effectiveness.

[0009]

[Means for Solving the Problem] According to this invention, it is CuO/SiO_2 of oxide criteria. The range of 0.5 thru/or 2 has the mol presentation to express, and the amorphous silicic-acid copper whose oil absorption a BET specific surface area is 50 thru/or 120ml / 100g in 100 thru/or 300m² / g and whose elution volume of the copper ion by the aqueous ammonia of 1 convention is 1% or less per all Cu(s) is offered.

[0010] According to this invention, it is SiO_2 again. To the alkali silicic-acid water solution whose solid content concentration is 0.1 thru/or 6 % of the weight, it is the water solution of copper salt CuO/SiO_2 By the quantitative ratio from which a mol presentation serves as the range of 0.5 thru/or 2 the bottom of temperature 20 thru/or a 60-degree C condition -- and the manufacture approach of the amorphous silicic-acid copper characterized by pouring into the bottom of churning and rinsing the product obtained on condition that pH6.5 thru/or 8.5 is offered so that the reaction termination pH may turn to 6.8 thru/or 7.5.

[0011] In another mode of this invention, the antimicrobial agent which contains the above-mentioned amorphous silicic-acid copper, and changes is offered. In still more nearly another mode of this invention, the antifouling paint which contains a paint film

formation resinous principle and the above-mentioned amorphous silicic-acid copper, and changes is offered.

[0012]

[Function] The silicic-acid copper by this invention is CuO/SiO_2 of oxide criteria. As a mole ratio is in the range of 0.5 thru/or 2, the content of a copper component is high concentration, and moreover, an amorphous thing is the important description.

[0013] CuO/SiO_2 To being the mineral of crystallinity [silicate / which has a mole ratio in above-mentioned within the limits / well-known / colla tempestade / (chrysocolla) / a shattuckite plan HEAITO JIOPUTEZU / both / chrysoprase], the silicic-acid copper by this invention is amorphous, and it is clearly different. Accompanying drawing drawing 1 is the X-ray (Cu-Kalpha) diffraction figure of the amorphous silicic-acid copper (example 1) by this invention.

[0014] Even if the specified substance of this invention is amorphous, it is silicic-acid copper and can check that it is not the mixture of an amorphous silicic acid and copper hydroxide (II) from an infrared absorption spectrum, an aqueous ammonia extract, a hue, etc.

[0015] Drawing 2 is the infrared absorption spectrum (IR) of A. copper hydroxide (II), the amorphous silicic-acid copper (example 1) by B. this invention, and a C. amorphous silicic acid. From this IR Fig., with the amorphous silicic-acid copper by this invention The characteristic peak by copper hydroxide (II), for example, the peak of wave number 692cm^{-1} , does not appear. Moreover, the thing which the peak of wave number 1087cm^{-1} based on the stretching vibration of Si-O of an amorphous silicic acid has shifted to the wave number 1005 thru/or 1025cm^{-1} , And since the peak of 804cm^{-1} peculiar to an amorphous silicic acid has disappeared, it turns out that copper hydroxide and an amorphous silicic acid are not contained on parenchyma, and the silicic-acid copper in which these carried out the chemical bond is generated.

[0016] Moreover, although the copper ion of isolation reacts with ammonia, it becomes complex ion and elution is carried out easily, with the amorphous silicic-acid copper of this invention, the elution volumes of the copper ion by 1 convention aqueous ammonia are 1.5% or less of all Cu components, and it is checked that the copper ion has combined with the silicic acid. Moreover, it is shown that this amorphous silicic-acid copper presented the hue of a bluish green color, and the copper ion has combined it.

[0017] In relation to the silicic-acid copper by this invention being amorphous, a BET specific surface area is comparatively as large as $100\text{-}300\text{m}^2/\text{g}$, and since it is discovered through a silicic-acid copper grain child's front face, an antibacterial action is desirable in respect of an antibacterial action. Moreover, as compared with the

above-mentioned specific surface area, oil absorption is a little small and has become 50 thru/or 130ml / 100g with the suitable range in respect of combination in resin or coatings.

[0018] Furthermore, as shown in the elution diagram by 1 convention aqueous ammonia of drawing 3, this silicic-acid copper has sustained-release [of a copper component], and is excellent also in the durability of an antibacterial action. In addition, the solubility in the range of pH 6-8.5 is 1 ppm or less as Cu ion.

[0019] Although the amorphous silicic-acid copper of this invention is manufactured by the double decomposition in the inside of the aqueous medium of water-soluble copper salt (II) and silicic-acid alkali, it is important for this double decomposition reaction to pour the water solution of copper salt gradually and to perform it into a silicic-acid alkali water solution. In having poured silicic-acid alkali into the water solution of copper salt conversely, the amorphous silicate of this invention cannot be obtained as shown in the example 2 of a comparison mentioned later.

[0020] This one side pouring reaction is faced and it is SiO₂ in silicic-acid alkali. It is appropriate for concentration that it is in 0.1 thru/or 6% of the weight of the range, and when it is except the above-mentioned range, it has the inclination for the yield of the silicic-acid copper of 0.5-2 to fall [CuO/SiO₂ mole ratio], or for a presentation to become an ununiformity. If 20 thru/or the range of 60 degrees C are suitable and lower than this range, double decomposition will not advance smoothly, and when reaction temperature is higher than this range, it has the inclination for a presentation to become an ununiformity. also performing a pouring reaction so that pH at the time of reaction termination may serve as the range of 6.8 thru/or 7.5 -- important -- Above pH -- if out of range, there is an inclination for the rate of an unreacted copper component (copper component of isolation) to increase. Although it is necessary in a reaction mixture to carry out rinsing removal of these salts since the alkali-metal salt of the anion of copper salt is generating, pH at the time of this rinsing is also important when preventing that a copper component separates, and an isolation copper component increases [pH] except the above-mentioned range.

[0021]

[Best Mode of Carrying Out the Invention] In this invention, although either can be used if it is water-soluble copper salt (II), inorganic-acid salts, such as a copper nitrate, a copper sulfate, and a copper chloride, and organic-acid salts, such as copper acetate, are suitable. the concentration of water-soluble copper salt -- 3 -- or especially 4 thru/or 35% of the weight of the range is suitable 60% of the weight.

[0022] As silicic-acid alkali, a sodium silicate, a potassium silicate, etc. are used,

especially M is alkali metal among formula $MO \cdot nSiO_2$ type, and that in which n has the number of 2 thru/or 3.5 and the presentation of ** which is especially the number of 2.6 thru/or 3.5 is used.

[0023] as for pouring of this copper salt, the whole is maintained by homogeneity although the pouring reaction of the water-soluble copper salt to the inside of a silicic-acid alkali solution is performed to the bottom of the condition mentioned above -- as -- the bottom of sufficient churning -- and it is good to carry out so that pouring may be completed by about 1/2 thru/or 1/8 of overall reaction time amount. After pouring termination, a reaction mixture is maintained in said temperature requirement, and it is good 0.5 thru/or to ripe for about 10 hours.

[0024] It filters, rinses and dries and grinds as occasion demands, and a reaction termination happiness-in-the-next-life product is classified, and let it be a product. Although rinsing should be performed on the conditions mentioned above, it is desirable that the temperature at the time of rinsing is also the same temperature as reaction temperature, and it is good to rinse so that the electric resistance of a washings may become more than 10,000-ohmcm. The desiccation in an elevated temperature from which disassembly of silicic-acid copper produces desiccation should be avoided, and, generally 100 thru/or desiccation at 150 degrees C are appropriate for it.

[0025] Although the amorphous silicic-acid copper by this invention is the particle of an indeterminate form as it is shown in the scanning electron microscope photograph of drawing 4, generally the particle size is a volume criteria median size, and is good 0.2 thru/or for there to be 10 micrometers especially in 0.2 thru/or the range of 5 micrometers. Bulk density is 0.5 thru/or 0.8g/ml, and this amorphous silicic-acid copper has pH when considering as 25-degree C 5% aqueous suspension in the range of 6 thru/or 8.5. In order that this amorphous silicic-acid copper may raise particle properties, a pigment property, dispersibility, a surface characteristic, etc., various inorganic materials, an organic material, etc. can be used for it, and reforming processing can be carried out.

[0026] as an inorganic material -- for example, at least one sort, such as detailed amorphous silica, such as Aerosil and colloidal silica, a detailed alumina, a detailed titania, and a calcium carbonate, -- sprinkling (outside **) -- it can blend and the fluidity and dispersibility can be raised. The loadings have 0.01 thru/or 10% of the weight of the good range.

[0027] Moreover, as an organic material, a higher fatty acid, metal soap, a silane coupling agent, a titanium coupling agent, various waxes, and a surface active agent

can be coated, and the dispersibility to the inside of plastic paint can be improved. Although the amount is different with extent or application of reforming, 0.001 thru/or 5% of the weight of the range are suitable for it.

[0028] Paper, wood, various textiles, various coatings, a plastic, etc. are made to contain the amorphous silicic-acid copper of this invention with means, such as spreading, sinking in, and combination, and it is applicable to manufacture of an antibacterial product. Moreover, this amorphous silicic-acid copper can be blended with various coatings, for example, vinyl chloride resin, vinyl chloride-isobutyl ether copolymerization resin, chlorinated-rubber resin, chlorination polyethylene resin, acrylic resin, styrene-butadiene system resin, epoxy system resin, polyester system resin, petroleum system resin, ROJIE ester system resin, tributyl tin content acrylic copolymerization resin, silicone rubber, etc., and can be used as an antifouling paint. It is good for such an application 5 thru/or for especially the amorphous silicic-acid copper of this invention to use in 10 thru/or 30% of the weight of an amount 60% of the weight.

[0029]

[Example] The following example explains this invention. In addition, measurement of powder physical properties and an evaluation trial of amorphous silicic-acid copper were based on the following approach.

(1) It measured in Cu-Kalpha using the RAD[by X-ray-analysis Rigaku Corp.]-IB system.

(2) It was based on hue viewing.

(3) QUANTA by specific-surface-area Yuasa Ionics The BET specific surface area was measured using SORB.

(4) Oil absorption JIS It was based on K-5101.

(5) Bulk density (based on an Ishiyama style specific volume test method.)

After balance picking and the Ishiyama chemical machinery factory specific volume tester performed the fall impact for 2.5g of samples in the test tube with 20ml graduation for 20 minutes, the volume was read to 0.1ml and bulk density was computed by the degree type.

(6) 5g of pH samples was added to 200ml beaker balance picking and 100ml of ion exchange water, it carried out the after [churning 2-hour neglect] ** exception for 10 minutes at 25 degrees C, and pH of filtrate was measured with the pH meter.

(7) It was based on the laser particle-size-distribution measuring method using LS130 mold machine made from median size coal tar.

(8) Cu was measured for the filtrate of Cu solubility above (7) with the atomic absorption method.

(9) It evaluated with the food-sanitation-hygiene inspection guide microorganism test handbook at the Niigata environmental sanitation lab of an antibacterial test Ministry of Health and Welfare assignment inspection institute.

[0030] [Example 1] 42g (product made from Hokuetsu Chemical industry) of sodium silicate No. 3 articles, 29.5g of sodium hydroxides of a reagent, and 500ml of ion exchange water Balance picking, You made churning ripe keeping at 30 degrees C, having made 250ml of ion exchange water add and dissolve 97g of reagent copper-nitrate 3 hydrates in 1l. another beaker, applying to said sodium silicate for 1 hour, being dropped at it, and keeping at 30 degrees C having put into the 1l. beaker and agitating, continuously [for 4 hours], and the product of a bluish green color was obtained. the suction filtration of the obtained slurry -- it carried out. pH of filtrate was 7.1 and Cu was 0.15 ppm. Next, 1l. of 30-degree C ion exchange water was added, and the product was washed. The specific resistance of the place and penetrant remover which performed this washing actuation 6 times was [20100ohms of 7.1-8.2, and Cu(s) of cm and pH] 0.02-0.4 ppm. a washing termination cake -- 110 degrees C -- constant temperature -- it was made to dry with a drier, the small sample mill ground, and the bluish green color powder end of 3.0-micrometer median size was obtained.

[0031] [Example 2] 52g (product made from Hokuetsu Chemical industry) of sodium silicate No. 3 articles, 15.2g of reagent sodium hydroxides, It keeps at 50 degrees C, putting 600ml of ion exchange water into balance picking and a 1l. beaker, and agitating it. 300ml of ion exchange water was made to add and dissolve 62.4g of reagent copper-sulfate 5 hydrates in 1l. another beaker, it applied to said sodium silicate for 2 hours, and was dropped at it, and you made churning ripe keeping at 20 degrees C continuously [for 5 hours], and the product of a bluish green color was obtained. Suction filtration of the obtained slurry was carried out. pH of filtrate was 6.9 and Cu was 0.2 ppm. Next, 1l. of 50-degree C ion exchange water was added, and the product was washed. 23300ohms of cm, pH7.5, and Cu(s) of the specific resistance of the place which repeated this washing actuation 7 times, and a penetrant remover were 0.2-0.5 ppm. a washing termination cake -- 120 degrees C -- constant temperature -- it was made to dry with a drier, the small sample mill ground, and the bluish green color powder end of 3.5-micrometer median size was obtained.

[0032] [Example 3] 76g of reagent potassium-silicate solutions, 7.3g of reagent potassium hydroxides, and 400ml of ion exchange water were put into the beaker of 1l. of balance picking, you made churning ripe having made 550ml of ion exchange water

add and dissolve 25g of reagent copper acetate 1 hydrates in 1l. another beaker, applying to said potassium-silicate solution for 2 hours, being dropped at it, and keeping [having kept at 20 degrees C,] at 20 degrees C agitating, continuously [for 5 hours], and the blue product was obtained. Suction filtration of the obtained slurry was carried out. pH of filtrate was 7.4 and Cu was 0.2 ppm. Next, 1l. was added for 20-degree C ion exchange water, and the product was washed. 21000ohms of cm, pH8.4, and Cu(s) of the specific resistance of the place which repeated this washing actuation 6 times, and filtrate were 0.5 ppm. a washing termination cake -- 110 degrees C -- constant temperature -- it was made to dry with a drier, the small sample mill ground, and blue powder with a median size of 2.5 micrometers was obtained.

[0033] [an example 4] -- 52g (product made from Hokuetsu Chemical industry) of sodium silicate No. 3 articles and 24g of reagent sodium hydroxides are put into balance picking and a 1l. beaker, ion exchange water is added, and it is referred to as 500ml, and the churning dissolution is carried out and it maintains -- 94g of moreover, reagent copper-sulfate 5 hydrates -- a 1l. beaker -- balance picking and ion exchange water -- in addition, it is referred to as 500ml, and the churning dissolution is carried out and it maintains. It is kept different from these to 2l. beaker under 800ml balance picking of ion exchange water, and churning at 60 degrees C. Churning aging was carried out for 3 hours, being dropped at it, the sodium silicate solution and the copper-sulfate solution them over this for equivalent [every] 3 hours, and keeping at 60 degrees C, and the product of a bluish green color was obtained. [said] Suction filtration of the obtained slurry was carried out. PH of filtrate was 7.1 and Cu was 0.1 ppm. Next, 1l. of 60-degree C ion exchange water was added, and the product was washed. 25000ohms of cm, pH7.6, and Cu(s) of the specific resistance of a place and filtrate which repeated this washing actuation 7 times and performed it were 0.2 ppm. a washing cake -- 130 degrees C -- constant temperature -- it was made to dry with a drier, and ground by small Sun Bull, and the powder of a bluish green color with a median size of 3.1 micrometers was obtained.

[0034] [Example 1 of a comparison] The dropping reaction of the example 1 was carried out at 80 degrees C, and the powder of the place and black green which performed the same actuation as the following was obtained.

[0035] [Example 2 of a comparison] The powder of the place and ashes green which performed same actuation was obtained except having made the copper-sulfate solution carry out the dropping reaction of the sodium silicate solution for an example 2.

[0036] [Example 3 of a comparison] 4.2g (product made from Hokuetsu Chemical industry) of sodium silicate No. 3 articles, and 38g of reagent sodium hydroxides and

500ml of ion exchange water are put into balance picking and a 1l. beaker, and it keeps at 30 degrees C under churning. Made 300ml of ion exchange water dissolve 120g of reagent copper-nitrate 3 hydrates in another beaker, applied to said sodium silicate solution for 1.5 hours, and were dropped at it, and it was made to ripe under 2-hour churning, keeping at 30 degrees C, and the product of ashes green was obtained. Suction filtration of the obtained slurry was carried out. pH of filtrate was 7.5 and Cu was 0.4 ppm. The same actuation as an example 1 was performed below, and the powder of black green was obtained.

[0037] The result of the antibacterial trial of powder physical properties to Table 1 is shown in Table 2.

[0038]

[Table 1]

[0039]

[Table 2]

9ml of Test-1:sterilization physiological salines -- 1g of each specimen -- putting in -- ten dispensing solutions -- carrying out -- this from -- 50 dispensing solutions were made and 0.5ml was used.

9ml of Test-2:sterilization physiological salines -- 1g of each specimen -- putting in -- ten dispensing solutions -- carrying out -- this from -- 150 dispensing solutions were made and 0.5ml was used.

[0040] [Example 5] It blended with the long-oil-alkyd-resin coating 100 section at a rate of the amorphous silicic-acid copper powder 30 section of this invention obtained in the example 1, and distributed by the day spur for 20 minutes. Viscosity added and prepared thinner and obtained the antifouling paint. 2mm in thickness, and area 1m² It applied to the front flesh side, the antifouling paint prepared to the square griddle as above-mentioned was further applied, after hardening by drying, and it was applied twice. This antifouling paint spreading plate was stood to the place with a depth of about 2m from the seashore, it was immersed for six months all over seawater, and the adhesion condition of a living thing was observed for every month supposing the operation conditions of a vessel. The occupancy area (%) of the living thing to a whole griddle surface product estimated the engine performance. The griddle which applied the coating which does not blend silicic-acid copper as Blank on the same conditions as

the above was put in order and stood. A result is shown in Table 3.

[0041]

[Table 3]

[0042]

[Effect of the Invention] According to this invention, they are copper salt water solutions, such as a copper nitrate, to an alkali silicic-acid water solution CuO/SiO_2 . The amorphous silicic-acid copper which has a new property is obtained by pouring into the bottom of a condition 60 degrees C or less so that a mol presentation may serve as the range of 0.5 thru/or 2. It can use effective in a cheap antimicrobial agent or an antifouling paint, using an operation of Cu ion, since it is the fine particles which this amorphous silicic-acid copper has a BET specific surface area comparatively as large as 100 thru/or 300m² / g, and whose oil absorption is 50 thru/or 130ml / 100g, and were excellent in pigment nature in comparison, and the solubility of a copper ion is low, environmental standards are fully satisfied and Cu ion is moreover gradually emitted by the aquosity medium system.

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